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DMIC review OF RECENT DEVELOPMENTS

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Corrosion and Compatibility

W. E. Berry • March 4, 1970

ALUMINUM ALLOYS

Stress-Corrosion Cracking

The factors affecting the initiation of stress-corrosion-cracking behavior in thick plate of 2219, 7039, 7075, 7C79, and X7375 aluminum alloys have been studied by Alcoa.(1) In 7079-T6 alloy, cracks initiated on grain boundaries at pits from which Mg_2Si particles had been dissolved. Cracks initiated at random sites on grain boundaries of the other alloys. The stress-corrosion cracks propagated along grain boundaries in the straightest possible paths perpendicular to the stress. These paths were series of recrystallized grain boundaries in the 2219 alloy, and were boundaries developed during several stages of hot working of the ingot in the 7075-T6, 7079-T6, and 7039-T6 alloys. Other findings indicated that dislocations, dispersoids, and zone-type precipitates had no apparent effect on crack initiation. Precipitate particles on boundaries had no direct effect on crack initiation, although their formation in the 2219 and 7075 alloys was accompanied by copper depletion adjacent to the grain boundaries, which provided anodic regions in which cracks initiated. Chemically produced pits and mechanical abrasion did not act as crack-initiation sites.

Alcoa also has investigated the mechanism of stress corrosion of aluminum alloys.(2) A similarity in stress-corrosion behavior between 7075-T6 alloy and 7039-T63 alloy was obtained by quenching thin sections of 7075-T6 at a rapid rate. In electrochemical tests, the most anodic phase involved in the stress-corrosion process was found to have the same potential in each alloy; however, the potential of the most anodic phase involved in the stress corrosion of less rapidly quenched 7075-T6 alloy was appreciably less negative. The similarity in stress-corrosion behavior of 7039-T63 and rapidly quenched 7075-T6 was attributed to the copper content of the M-phase in 7075-T6. As the quenching rate of 7075-T6 is increased, the copper content in the M-phase of this alloy decreases; as the M-phase approaches its limiting composition of $MgZn_2$, the stress-corrosion behavior of 7075-T6 approaches that of 7039-T63.

A study of the mechanism of stress corrosion of aluminum alloys has also been completed by Tyco Laboratories.(3) In the Al-Cu system (e.g., 2219), stress-corrosion susceptibility was found to be associated with paths at the grain boundaries which were preferentially attacked by corrosion. In the Al-Mg-Zn-Cu systems (e.g., 7075), there was little correlation of stress-corrosion susceptibility with specific corrosion properties. Instead, there was a strong correlation with mechanical properties and with the tendency for cleavage to occur along the grain boundaries. Onset of stress corrosion was believed to be delayed by mechanical deformation in a layer at the surface of the metal which destroyed the grain-boundary structure. Mechanical deformation followed by anodic dissolution was recommended as a method for improving resistance to stress-corrosion cracking. Other suggestions to effect improvement were to slow the quenching rate (quench in oil) but retain strength, and, by a combination of thermal and echanical treatments, to destroy the well-defined grain-boundary structure in the bulk of the metal.

General Corrosion

An accelerated laboratory test to determine the exfoliation corrosion resistance of aluminum alloys has been described by Reynolds Metals Company.(4) The test consists of a 1-week exposure to an alternate salt spray (30 minutes) and 100 percent humidity (1 hour) cycle at 120 F. The salt-spray cabinet complies with ASTM B117-64. The test solution consists of 4.2 percent synthetic sea salt solution [ASTMD 1141-52 (1965)] which has been acidified by adding 1 volume percent glacial acetic acid (pH 2.8). Excellent correlation is claimed between the accelerated test and service performance of unalloyed aluminum and the Al-Cu, Al-Zn-Mg-Cu, Al-Zn-Mg, Al-Mn, Al-Mg, and Al-Mg-Si aluminum series.

The rapid corrosion of aluminum-copper alloys by CH_3OH + CCl_4 mixtures has been investigated by South African scientists.(5) The reaction products were found to be finely divided copper, CuO, $AlCl_3$, $CuCl_2$, chloroform ($CHCl_3$), tetrachloroethylene (C_2Cl_4), formaldehyde (CH_2O), hexachloroethane (C_2Cl_6), hydrogen, some methane (CH_4), and possibly some ethane (C_2H_6). The following reactions were proposed: the CCl_4 dissolves the copper from the alloy to form $CuCl_2^-$ and $[CuCl_4]^{2-}$; Cl^- from the CCl_4 causes local breakdown of the protective oxide film on the aluminum; $CuCl_2^-$ ions are then discharged on the aluminum and the resulting copper deposits set up localized galvanic cells; CCl_4 is reduced at these copper cathodes; the reaction between aluminum and CH_3OH produces hydrogen and formaldehyde (CH_2O) at the anode; $AlCl_3$ is one of the reaction products as well as C_2Cl_6, which is probably formed from the combination of the free radicals ($\cdot CCl_3$).

FERROUS ALLOYS

Steels

Much of the current knowledge involving the corrosion of steel piling in seawater has been presented in a literature survey prepared by the [illegible] Engineering Research Center.[6] Included in the report are the causes of corrosion, effects of environmental conditions, corrosion rates of bare steel, test results on protective coatings, the use of cathodic protection, and the use of concrete jackets for protection. The survey indicated that flame-sprayed zinc sealed with Saran or vinyl is possibly the best coating system tested; properly designed and constructed concrete jackets are very effective; cathodic protection is also effective; and combinations of cathodic protection with coatings or concrete jackets may be advantageous.

The University of Michigan has confirmed the excellent resistance to cavitation of a 0.25C-13Cr-10Mn steel initially reported in Eastern European literature.[7] Tests were conducted for 44 hours in 120 F tap water at a frequency of 20 kHz and an amplitude of 2 mils. The high-manganese, high-chromium steel was 15-fold better than Type 304 stainless steel in these tests. The alloy was reported to have an unstable austenitic structure after air cooling from 1100 C (2010 F). Apparently, the intense microimpacts characteristic of cavitation caused the unstable austenite to transform to martensite plus some epsilon phase both of which are hard and resistant to further erosion.

The plane-strain stress-corrosion threshold K_{ISCC} and fatigue-crack growth rate of a high-strength martensitic stainless steel, AFC 77 (14Cr-13Co-5Mo), were studied at Boeing.[8] Tests were conducted in air and in 3.5 percent NaCl solution. The K_{ISCC} was lowered as the tempering temperature was increased from 500 to 1100 F and as the amount of cold work was increased from 10 to 20 percent in strain-aged specimens. Retained austenite in the microstructures raised the K_{ISCC} at tempering temperatures of 500 through 1000 F. (The latter was the highest temperature at which austenite was retained.) Fatigue-crack growth rates were at a maximum in both dry air and 3.5 percent NaCl solution for material tempered at 700 F. Retained austenite reduced the fatigue-crack growth rate in NaCl solution, but increased it in dry air under the conditions studied.

The Naval Research Laboratory has examined specimens from a 1250-foot length of Type 304 stainless steel wire rope after 34 months' continuous immersion in the Gulf of Mexico.[9] The absence of corrosion on the top 1000 feet of the stainless steel wire rope was attributed to the beneficial effects of a retained lubricant, to cathodic protection from a steel anode located above the rope, and to probable inadvertent cathodic protection from the 6062-T6 aluminum surface buoy. Relatively severe corrosion was observed on the bottom 250 feet of the rope where it was shielded from cathodic protection because it had been jacketed with Neoprene to prevent abrasion of the synthetic rope used for the lower section of the mooring system.

Laboratory tests conducted by Combustion Engineering and The Ohio State University have shown that sensitized Types 304 and 316 stainless steel will exhibit intergranular attack in water containing fluorides providing one or more of the following conditions exist: (1) applied or residual tensile stress; (2) cold work, with or without macro stress; (3) a crevice; (4) visible oxide film formed by exposure to air at elevated temperature.[10] Intergranular attack occurred over the temperature range of 80 to 180 F, at levels of pH 4.96 to 10.45, and at fluoride levels of <1 to 542 ppm. The above conditions did not cause intergranular attack of sensitized Inconel 600, Incoloy 800, Type 304L stainless steel, Type 347 stainless steel, and austenite-ferrite weld deposits or castings.

The failure of Type 347 stainless steel tubes in regeneratively cooled thrust chambers of booster engines using nitrogen tetroxide and Aerozine-50 has been studied by the Aerospace Corporation.[11] The tubes did not fail under classical burnout conditions. Instead, carburization and nitriding caused not only loss of ductility, but also loss of metal on both the internal (fuel-oxidizer) and external (combustion gases) surfaces of the tubes and eventual failure by pinholing or cracking. The external surfaces were carburized by the combustion gases. The internal walls were both carburized and nitrided by the decomposition products of the Aerozine-50 (50/50 hydrazine/unsymmetrical dimethyl hydrazine).

NICKEL-BASE ALLOYS

The mechanism of sulfidation of nickel-base superalloys was investigated by United Aircraft Research Laboratories.[12] Aqueous solutions of saturated Na_2SO_4 were evaporated to dryness on test specimens, and the specimens were then exposed to flowing oxygen at high temperatures. Sulfidation occurred in those alloys that formed alumina-rich surface scales. The Na_2O which is in equilibrium with Na_2SO_4 is believed to react with and disrupt the alumina-rich scale. The Na_2SO_4 then reacts with the substrate to form the sulfide phase associated with sulfidation attack. Na_2O is a product of this reaction which prevents re-formation of a protective oxide scale, and thus oxidation of the alloy is accelerated. The oxides of chromium, tin, and samarium were found to inhibit sulfidation attack.

TITANIUM ALLOYS

The effect of surface preparation and exposure variables on the hot-salt stress-corrosion cracking of Ti-8Al-1Mo-1V alloy has been studied at Lewis Research Center.[13] The inside bore of tubular tensile specimens was coated with NaCl and the specimens were stressed at 10,000 to 115,000 psi and exposed to flowing air at 600 to 800 F for 96 hours. They were then pulled in tension to determine loss in ductility (embrittlement) and establish the threshold stress level below which no embrittlement occurred. Stress-relieved specimens exhibited drastically lower threshold stresses than did as-machined specimens. Threshold stress was increased by increasing the air flow, increasing the air pressure, and precoating with salt at high temperatures (600 to 800 F). Threshold stress was unaffected by changing the salt concentration from 0.2 to 2 mg/in.^{2} on the specimen surface. Threshold stress was lowered by increasing the exposure time from 96 to 235 hours.

The stress-corrosion cracking of both alpha- and beta-phase titanium alloys in methanol-chloride solutions has been studied by North American Rockwell Corporation.[14] Cracks were transgranular

and intergranular, depending on alloy chemistry, grain size, degree of prior cold work, and loading conditions. Crack-propagation velocities were 10^{-3} cm/sec for intergranular failure and 10^{-2} cm/sec for transgranular failure. The alpha-phase alloys Ti-50A and Ti-75A cracked at potentials more positive than -250 mv (Ag/AgCl standard electrode), while the alpha-beta alloy cracked at potentials more positive than -1000 mv. The results indicate that the intergranular failures cannot be explained on the basis of anodic dissolution alone, while the transgranular failure cannot be explained by anodic dissolution or brittle-film rupture mechanisms but is apparently associated with a lowering of the required normal stress for cleavage due to the environment.

PROTECTIVE COATINGS

Various elastomers and the design aspects of fasteners have been studied by Vought Aeronautics in an attempt to alleviate the problem of fasteners breaking the protective films applied to exterior areas of aircraft.(15) Laboratory tests at room temperature and -65 F revealed that silicone, polyurethane, and polysulfide elastomers resisted rupture better than the epoxy finish now in use. Use of radiused countersink and elimination of fastener protrusion above the skin surfaces were found to accommodate a continuous film at the countersink edge and minimize film rupture at the fastener edge.

An extensive study of the corrosion behavior of electrodeposited chromium coatings on steel has been made by Polish scientists.(16) A comparison was made of the corrosion behavior of four kinds of coatings at six coating thicknesses (0.5 to 54 μ), and in five accelerated corrosion tests. From the results of the tests, the corrosion resistance of electrodeposited chromium on steel was concluded to be relatively poor at coating thicknesses below 8 microns and improved considerably at thicknesses greater than 18 microns.

MISCELLANEOUS

A variety of materials have been evaluated for turbine buckets at temperatures to 2200 F in a study conducted by the International Harvester.(17) Specimens were evaluated on the basis of cyclic oxidation, oxidation-erosion/thermal fatigue, and physical and mechanical properties. The major limitations of the materials evaluated were low strength and poor impact resistance. The future potential of the various classes of materials for use in turbine buckets at 2200 F or higher was rated as follows:

- Good -- coated refractory metals and coated carbon composites
- Fair -- metal-matrix fiber-reinforced composites
- Poor -- intermetallic compounds, laminated composites, cermets, dispersion-strengthened superalloys, and superalloys.

Studies on the mechanisms of sand and dust erosion in gas-turbine engines are continuing at Solar.(18) Dust varieties representative of American and Southeast Asia theaters of operations are being used. With Arizona road dust, increasing particle size and increasing velocities increased the amount of erosion. The critical threshold velocity above which erosion occurred at 0 to 43-μ particle size was 105 and 153 fps, respectively, for 2024 aluminum and Type 410 stainless steel targets. Pleiku laterite dust caused no erosion over the particle-size range studied (0 to 147 μ) and velocities to 830 fps. Dust accumulated on the surface and apparently functioned as protective film. Scanning-electron-microscope studies of heavily eroded surfaces (Arizona road dust) revealed a semimolten surface containing many micron- and submicron-size metallic particles and a sizable number of embedded dust particles.

Examples have been cited of current failure-analysis investigations conducted by the Materials Support Division of the Air Force Materials Laboratory.(19) Included in the investigations are the systems service history, information obtained through metallurgical examinations, illustrative photographs, reasons for cause of failure, and recommended corrective action. Failures included stress-corrosion cracking of a 7079-T6 aluminum wing-tank piston cylinder, a 2014 aluminum missile fuel tank, and a 7075-T6 aluminum Lunar Module strut; fatigue failure initiating at a fastener hole in a lower front-wing spar, at a fastener in a 7075-T6 aluminum splice-plate piece, in a webbing of a 7075-T6 aluminum wing carrythrough forging, on the side of a Greek Ascoloy compressor blade, and in a first-stage compressor fan blade; and overload failures in a 4140 steel rudder actuator piston, an H-11 steel tail-rotor drive coupling, and a steel pump-shaft component in a ground-support item.

The use of standards in corrosion control is discussed in a paper by a New Zealand scientist.(20) Reference is made to British, Australian, and American standards on corrosion of metallic materials as they apply to design, choice of materials, control of environment, surface preparation, metallic coatings, nonmetallic coatings, cathodic protection, and anodic protection. Test methods quoted in many of the standards also are briefly discussed.

Nondestructive methods of measuring residual stress in components are discussed and evaluated in a recent paper issued by Harwell of the U.K. Atomic Energy Research Establishment.(21) These methods include X-ray crystallography, ultrasonic birefringence, ultrasonic surface waves, ultrasonic goniometry, ultrasonic-beam interaction, magnetostriction, magnetoabsorption, and the Barhausen noise effect.

A portable, thermal, nondestructive system suitable for inspecting large structures, such as aircraft, in the field has been designed, built, and tested by Automations Industries.(22) The system detects near-surface material and structural defects such as corrosion, voids, delaminations, unbonds, and inclusions. It consists of a hand-held scanning head, operator's control console, and interconnecting cable. The head contains the hardware and electronics to sequentially heat and scan the surface temperature of the material. Defects that lie under the surface are detected as a change in surface temperature over the defect area.

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